

Tribocharging phenomena in hard disk amorphous carbon coatings with and without perfluoropolyether lubricants

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ABSTRACT

Scanning polarization force microscopy was used to study changes in surface potential (tribocharging) caused by the contact between a tungsten carbide tip and the amorphous carbon coating of a hard disk, both when bare and when covered with Zdol-TX lubricant. The surface potential change produced by tip contact decays with time at a rate that is strongly dependent on lubricant coverage, and on the presence of oxygen and water vapor in the environment. Two different charging mechanisms are proposed. One involves chemical modification of the surface by removal of oxygen bound to the surface. This gives rise to a potential change that decays with time. Another mechanism involves trapping of charge in states within the energy gap of the insulating carbon film. The potential change due to this trapped charge does not decay over periods \gg 1 hour.

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I. INTRODUCTION

The surfaces of magnetic hard disk media are protected by a hard amorphous or diamond-like carbon film to minimize wear during start-stop, and to prevent corrosion of the underlying magnetic material. On top of the hard coating, a molecularly thin film of lubricant is present to passivate against contamination, minimize friction, and help prevent corrosion. The lubricant must be non-volatile for long-lasting operation, bind strongly to the carbon surface, and have sufficient mobility to replenish areas where molecules were removed as a result of head-disk contact. High molecular weight perfluoropolyether (PFPE) polymers fulfill these requirements.¹ In order to improve surface bonding, the PFPEs are usually modified with specific functional end groups.

The continuous increase in data storage capacity of hard disks requires a reduction of the head-disk spacing. Obviously this will lead to an increase in head-disk interaction and will thus require even more protective capabilities of the PFPE lubricant and hard carbon film. In addition, while the carbon layer becomes thinner and thinner, it must remain non-porous and should not be easily damaged in order to keep its protective capabilities against corrosion. The interaction between PFPE films and carbon surfaces has been extensively studied.²⁻⁵ Also, the tribological properties of PFPE films as a function of thickness⁶ and advanced additives⁷ have been studied. However, little is known about the effect of head-disk contact on the carbon coating underneath the lubricant layer.

A recently developed technique called scanning polarization force microscopy (SPFM)⁸ is ideally suited for this kind of study. With SPFM, one can study both liquid and solid surfaces with a lateral resolution on the nanometer scale and a vertical resolution of the order of 1 Å. The technique uses electrical forces between a sharp conductive tip and the surface for non-contact imaging in an atomic force microscopy (AFM) apparatus. A sinusoidal voltage (typically 10 kHz, 10 V peak-to-peak, in this

work) is applied to the tip. When the tip is brought within a few tens of nanometers of the sample, it starts to interact with the sample surface and oscillates due to the attractive electrostatic polarization force between tip and sample. The deflection of the cantilever is measured by the laser-beam reflection method and, with the help of lock-in amplifiers, the ac response is separated into fundamental (1ω) and second harmonic (2ω) components. In general, the 1ω and 2ω amplitudes contain information on the surface potential and topography, respectively.^{9,10} By keeping the amplitude of the 2ω signal constant through feedback control, topography as well as surface potential distribution images can be simultaneously recorded. Recent examples of the application of SPFM include a study of the structure of water films formed on mica,¹¹⁻¹³ measurements of the effects of disjoining pressure on the condensation of glycerol,¹⁴ water adsorption and deliquescence at the surface of alkali halide crystals,¹⁵ and de-wetting of lubricant layers on hard disks.⁵

Here, we present the results of applying SPFM to studying changes in the surface potential caused by the contact between a tip and amorphous carbon films when bare and when covered with a perfluoropolyether layer. The changes in surface potential will be correlated with structural and/or electronic changes in the carbon film.

II. EXPERIMENTAL

Amorphous carbon films with a thickness of approximately 100 Å were deposited on NiP-coated aluminum hard disk substrates by means of dc magnetron sputtering. The disks were dip-coated in a diluted solution of Zdol-TX in a dihydroperfluoropentane (Vertrel-XF, DuPont) solvent. The average lubricant thickness was dependent on the concentration of the Zdol-TX solution and the withdrawal speed. Zdol-TX is a PFPE-type lubricant, with a backbone structure of the form: $X\text{-CF}_2\text{-}[(\text{O-CF}_2\text{-CF}_2)_n\text{-(O-CF}_2)_m]\text{-O-CF}_2\text{-X}$, with the functional end group $X = \text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-OH}$. The

hydroxyl end groups bind to the disk surface through the oxygen-lone pair orbitals. However, oxygen lone pair bonding is strongly suppressed for the fluorinated backbone due to steric hindrance.¹⁶ In our study, we used Zdol-TX with a molecular weight of 2500 g/mol and $m/n \sim 1.1$.

The average thickness of the lubricant overcoat was determined by ellipsometry. The lubricant coverage was always less than one monolayer ($\sim 18 \text{ \AA}$), since thicker layers tend to de-wet, creating droplets.⁵ Some of the dip-coated samples were treated using a standard wash-off procedure in Vertrel-XF solvent to remove Zdol-TX molecules that were not bonded to the carbon film. In some cases, to increase the coverage of the bonded lubricant layer, the dip-coated samples were baked at an elevated temperature (typically at $100 \text{ }^\circ\text{C}$ for up to an hour) before being degreased. No after-treatment was given to the other samples, resulting in a carbon film covered with both bonded and mobile lubricant.

Most of the experiments were performed in a SPFM setup housed in a humidity-controlled chamber. The relative humidity (RH) was controlled by flowing dry or water vapor-saturated nitrogen through the chamber. The value of RH was measured with an Omega RH-20C hygrometer. A few experiments were performed with a SPFM located in a vacuum chamber for better control of the pressure, humidity, and chemical composition of the gases inside the chamber.¹⁷ A silicon cantilever coated with tungsten carbide was used in all experiments. This lever is conductive¹⁸ and has a nominal spring constant of 1.1 N/m .

III. RESULTS

A. Contact potential changes induced by tip contacts

The contact between the AFM tip and the disk surface simulates a head-disk contact. In the experiments, we used a load of 50 nN , which produces a local pressure on the order of one GPa for typical tip radii. This is a realistic value to model head-disk

impact.

Figure 1(a) shows a $6 \times 6 \mu\text{m}$ SPFM topographic image of a carbon film covered by a 14.4 \AA thick bonded Zdol-TX layer. Before the SPFM image was taken, one contact mode scan with a grounded tip was performed at a load of 50 nN in the middle of the image over an area of $2 \times 2 \mu\text{m}$. No effects of this contact scan can be observed in Figure 1(a), indicating that the AFM tip did not remove the Zdol-TX layer during contact, or wear the substrate by more than 1 \AA . Only scratch marks, created by the polishing process of the carbon film, can be observed.

Figure 1(b) shows the simultaneously obtained SPFM surface potential image. The surface potential of the area where the tip contacted the surface is clearly different from the surrounding area. This indicates that, although no topographical changes in the overlying lubricant layer can be observed, the carbon film has been affected by the tip-disk contact. The tip has clearly changed the local surface potential while moving over the surface, a phenomenon that can be called tribocharging. We know from previous work that, at the applied load, the tip penetrates through the Zdol-TX layer and makes contact with the carbon film.⁵ The displaced lubricant molecules refill the hole after the tip is withdrawn. We believe therefore that the changes occur in the carbon and not in the lubricant layer.

Some of the scratch marks from the polishing process can vaguely be observed in Figure 1(b). This is due to a small coupling between the 2ω and 1ω channels from the limited gain in the feedback loop. It disappears at high gain.

To get more insight into the nature of the surface potential change, we have performed a number of experiments in which the surface potential was studied as a function of time in both lubricated and unlubricated surfaces. In these experiments, we specifically looked at the effect on the surface potential of the relative humidity (RH), lubricant coverage, and chemical contents of atmospheric gases.

Figures 2(a) and (b) show the evolution of the surface potential as a function of

time on an unlubricated amorphous carbon film at relative humidities of 20% and 50%, respectively. The data represent the surface potential difference with respect to the area outside the $2 \times 2 \mu\text{m}$ square where tip-disk contact occurred. The surface potential change is always found to be positive relative to the unmodified area. We observe that part of the surface potential decays over time, while another part remains constant on a time scale of hours. SPFM images show that the size of the area where the surface potential has been changed remains constant, *i.e.*, no spreading or shrinking takes place. In the plots, the origin of time axis corresponds to the time of initial tip-disk contact. The first data were obtained about 12 minutes after contact, since some time was needed to switch from contact mode to SPFM mode and to calibrate the surface potential. The measured data are in excellent agreement with an exponential-decay-plus-offset model of the form $a + b.exp(-t/\tau)$. The absolute value of the surface potential, at a given humidity and time after contact, and the offset value varied by a factor of almost two between different experiments. However, at a given relative humidity, an excellent reproducibility of the time constant τ was obtained throughout all experiments. If we compare the time constants at RH = 20% and at RH = 50%, we observe that the charge decay of the surface potential is significantly faster at a higher humidity ($\tau = 0.39$ and 0.24 hours, respectively). Experiments were also performed at RH = 80%. However, the absolute value of the surface potential was already very small by the time of the first measurement point, and the decay was too fast to obtain a reliable measurement.

In Figures 3(a) and (b), the course of the surface potential over time is shown on a carbon film covered by a 14.4 \AA thick bonded Zdol-TX layer, at a relative humidity of 20% and 50%, respectively. As pointed out previously, in this case, the weakly bound molecules had been removed by washing in Vertrel-XF solvent. The values of the constant τ were 0.93 and 0.43 hours, respectively. Again, the fastest charge decay is observed at the highest humidity. The values, however, are larger than for the bare surface, indicating that the bound Zdol-TX molecules have an appreciable effect in

slowing down the surface potential decay. Experiments at $RH = 80\%$ could not produce a reliable value of the time constant, for the same reasons as mentioned for the bare carbon surface. The previous results are summarized in the semi-logarithmic plot shown in Figure 4, which were obtained after subtracting the offset values from the data in Figures 2 and 3.

We also studied the surface potential decay on a carbon film covered by a 16.6 \AA thick Zdol-TX layer at relative humidities of 20% and 50%. In this case, the sample was neither baked nor washed in Vertrel-XF solvent after dip coating, so that both the strongly and weakly bound lubricant molecules, in roughly equal proportions, are present and form close to a complete monolayer of coverage. Obtaining a reliable value for the exponential time constants on this surface turned out to be rather difficult. First, the absolute values of the initial surface potential, *i.e.*, the potential difference immediately after tip-disk contact, were much smaller than in the previous situations, indicating that the presence of mobile lubricant results in a significant reduction of the initial tribocharging effect. In addition, the surface potential decay was much slower than in the previous experiments—almost comparable to the noise level. However, from an analysis of a number of experiments on this surface, we may conclude that the time constant is always larger than one hour for $RH = 20\%$ and $RH = 50\%$.

B. Contact with a biased tip

In the previous experiments, contact was always made with a grounded tip. Under these conditions, the surface potential change is always found to be positive relative to the unmodified area. However, the modified surface potential can also be lower than the surrounding unmodified area if we use a negatively biased tip during the contact scan, as shown in Figure 5. In Figure 5(a), we observe that a contact scan with a negatively biased tip (-2 V) produced a darker area, indicating a lower surface potential. After taking this image, we switched the tip bias to a positive value ($+2 \text{ V}$) and scanned a larger area

covering the previously modified area. As can be seen in Figure 5(b), the scanned area appears to be brighter than the rest. The area in the center is still darker, but less negative than before. These results demonstrate that charge-transfer processes between the tip and the substrate, in addition to chemical modifications of the surface, play an important role.

C. Influence of the atmospheric composition

In order to elucidate the mechanisms responsible for the decay of the surface potential, we studied the potential of bare carbon films as a function of time under different atmospheric conditions. No potential decay was observed within several hours of when the experiments were performed under vacuum conditions at a base pressure of 30 mTorr. Leaking water vapor into the chamber to produce relative humidities of 50% and 75%, respectively, did not result in any decay either. Furthermore, the surface potential change after contact was smaller than in the dry situation. Leaking dry oxygen (100 mTorr, RH = 0%) did, however, produce a slow decay of the potential.

These observations together with the ones in humid air indicate that: (a) oxygen plays a crucial role in the decay of the surface potential; and (b) water facilitates the decay, but can not cause any decay by itself.

IV. DISCUSSION

Using SPFM, we have demonstrated that the contact between the tungsten carbide coated silicon tip and the amorphous carbon film of a hard disk results in a local change in surface potential (tribocharging). The spatial extent of the modified area remains constant with time, excluding the possibility that diffusion processes from the surrounding areas contribute appreciably to the decay of the local charge. We believe that the modifications occur exclusively in the carbon film, because the Zdol-TX lubricant layer is easily penetrated by the AFM tip, as we have shown in previous work.⁵ However,

no changes in the topography of the carbon surface larger than 1 Å occur as a result of the contact.

Part of the surface potential increase caused by the contact decays with time, while another part remains constant, *i.e.*, it can not be measured in periods \gg 1 hour. On surfaces with a complete coverage of lubricant (bonded plus mobile), the surface potential change caused by tip-disk contact is very small. If only the strongly bound part of the Zdol-TX monolayer covers the carbon film, a change in potential of around 100 mV is observed, followed by a slow decay. On the bare carbon surface, the potential change is somewhat larger (~150-200 mV) and its decay with time is faster. While decay of the potential only occurs in the presence of oxygen, water vapor is very effective in increasing the decay rate.

The results suggest that several different mechanisms are responsible for the observed changes in surface potential or tribocharging. The part that decays with time can be ascribed to chemical changes of the surface, probably involving the removal of oxygen bound to the surface by the tip, which creates a positive potential region. The presence of a layer of lubricant hinders both the removal of oxygen and the subsequent re-oxidation reactions with atmospheric O₂ and H₂O. The mechanism of these reactions is unknown at present.

In addition to the changes in surface chemistry, there are also other mechanisms which produce charges that decay very slowly with time. One such mechanism is charge trapping. This could occur at electronic traps in the energy gap of insulating regions of the carbon film under the surface. These traps, whose nature is not yet understood, can be charged perhaps due to work function differences between the tip and the surface. We have also seen that, by using biased tips, the sign of the charge can be controlled. The polarity dependent charge transfer described above lends support to this electronic trap model. The existence of electronic traps in other varieties of amorphous carbon coatings has been documented in field emission studies of flat panel displays.¹⁹

V. CONCLUSIONS

The combined use of contact AFM and non-contact SPFM allowed us to study the effect of tip-disk contacts, simulating head-disk contacts, on the structure of the carbon coating and the effect of lubricants. On bare surfaces and on surfaces coated with a layer of lubricant Zdol-TX containing only strongly bound molecules (14.4 Å thickness), a substantial electrical potential change is produced. Part of this potential change decays with time in wet atmospheres, with the decay increasing at higher humidities. Another part of the potential change appears to remain unchanged for periods well over several hours. Experiments done in vacuum reveal that no change in the potential takes place. A pure oxygen atmosphere does produce a decay of the potential, but pure water vapor does not. The presence of roughly one complete monolayer of lubricant Zdol-TX (16.6 Å), containing both strongly and weakly bound molecules, decreases substantially the change in surface potential produced by the contact. It also slows down substantially its decay with time.

These results favor a model where the changing (decaying) part of the potential change produced by contact is due to a chemical modification of the surface, probably involving the removal of oxygen bound to the surface. Another part of the potential change due to contact is long lasting (with a lifetime of many hours) and appears to be due to charge injection and trapping in electronic states in the gap of the insulating regions of the DLC coating.

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FIGURE CAPTIONS

FIG. 1. (a) $6 \times 6 \mu\text{m}$ SPFM topographic image of a hard disk surface covered by a 14.4 \AA thick Zdol-TX layer (all bonded). The tip of the AFM had been scanned over a $2 \times 2 \mu\text{m}$ region in the center, in contact with the surface with a load of 50 nN , which produced a pressure on the order of 1 GPa . No changes in the topography are observed. Residual scratch marks (dark lines crossing the image) from polishing are visible. The areas in between the marks are flat within 1 \AA . (b) Simultaneously acquired SPFM surface potential image. The $2 \times 2 \mu\text{m}$ area in the middle of the image, previously scanned in contact, shows an increased surface potential. In this image, the gray scale corresponds to a surface potential difference of 67 mV .

FIG. 2. Time variation of the surface potential contrast produced by tip contact on an unlubricated amorphous carbon film. The relative humidity in (a) is 20% and in (b) is 50% . The data represent the surface potential difference with respect to the area outside the $2 \times 2 \mu\text{m}$ square where tip-disk contact occurred. The equation inside the boxes are the functional fits shown by solid lines through the measured points. The units are mV for $V_{surf.}$ and hours for t .

FIG. 3. Same details as in Figure 2, for an amorphous carbon film covered by a 14.4 \AA thick Zdol-TX layer (all bonded), at relative humidities of (a) 20% and (b) 50% .

FIG. 4. Semilog plot of the surface potential data of Figures 2 (solid lines) and 3 (dashed lines), after subtraction of the offset values. The slope of each curve represents the exponential time constant.

FIG. 5. SPFM images showing changes due to surface potential variations after tip

contact in the central part (marked with a box). In the left image, the central square was scanned in contact with the tip biased at -2 V , which produced a negatively charged area (but no visible topographic changes). The image on the right was acquired after a larger contact scan (large box) with the tip biased to $+2\text{ V}$. The potential in the previously negative region has decreased considerably and the region between the two boxes shows a positive surface potential.